CATALYSIS IN FUSED SALT SYSTEMS

BY

NOEL EDWARD NORMAN

B.Sc.(Hons.), University of Western Australia, 1943
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

Ease of transport, temperature control and insensitivity to catalysis poisons are three advantages which fused salts may have as catalysis materials. Studies of the mechanisms of fused salt catalyses have not been reported in the literature and the choice of a melt for a particular reaction is at present empirical. An investigation of the nature of fused inorganic salts was made and fom this study, known cases of catalysis were shown to employ molecular type melts. No instances of the use of ionic melts were found. The reported cases of reactions employing molecular melt catalysts fall into three groups, (a) Friedel-Crafts reactions, (b) halogenation, and (c) polymerization of organic compounds.

To further develop the field, work was carried out with ionic type melts, with two objectives in mind, (a) to illustrate a proposition that a similarity may exist between the catalytic behavior of the cation in the melt and the same element in the form of the free metal, (b) as no crystal structure exists in these catalysts, a study of catalytic mechanisms may be simplified by the use of fused salt materials.

Three systems, employing fused salt catalysts were studied.

(a) The formation of hydocarbons from carbon monoxide and hydrogen.

(b) The decomposition of acetylene.

(c) The decomposition of alcohols, e.g. ethanol.

Theory

The highly specific action of different catalysts on reacting systems has led to the useful chemisorption theory. Langmuir has made the definite statement that the adsorbed molecules are held to the surface by ordinary valence forces. However,

other work indicates that Langmuir's postulates are rather to be regarded as referring to an ideal limiting case. In proposing the analogous behavior of the metal ions in a salt melt and the free metal catalyst, a purely "chemical" point of view has been taken.

The generally accepted theory of metals is that they may consist of positive atomic cores, arranged in a regular lattice, with the valence electrons moving freely among them. If an inorganic salt, on fusion, dissociates into cations and anions, then in the melt there will exist the same positively charged metallic ions as are found in the metal lattice. In the case of the melt, the ions will be in rather different surroundings and at least two obvious differences will exist, i.e.. (a) the metallic ions will be "diluted" by anions and (b) a rigid lattice no longer exists. The work of Emmett and Brunauer (1) on the diluting effect of promoters in solid catalysts and the investigations of Steacie and Elkin (2) on a molten metal catalyst, were used to show that these two differences in the surroundings of the metal ions may not be significant. Also, the chances of having a convenient spacing for a particular reactant or product molecule are enhanced with a molten salt and this may be important in cases where the lattice parameter of the metallic catalyst has been shown to be of consequence. In a salt melt, the metal ions and also any reactant-catalyst complex, can migrate across the surface of the catalyst.

Experimental

Work with carbon monoxide and hydrogen.

A mixture of these two gases obtained by cracking methanol was passed through the molten salt catalyst an dthen sampled for analysis. Difficulty was experienced in obtaining a melt with suitable melting point and composition characteristics. No useful catalyst was found for this reaction.

The decomposition of acetylene.

Tiede and Jenish (3) have published material grouping twenty nine metals according to their ability to decompose, or have no action at 600°C., on acetylene. Acetylene was passed through the halide melts of four metals from each of these groups and the behavior of the metals as ions was shown to be similar to their action in the free metal state.

The decomposition of ethanol.

Ethanol vapor was decomposed when bubbled through a cuprous chloride melt at temperatures between 400 and 500°C. The melt was shown to behave as a mixed catalyst and both dehydrogenation and dehydration reactions were induced. The dehydration reaction has been shown by Sabatier (4) to be produced by cuprous chloride below the melting point, but evidence is presented here to show that dehydrogenation reaction is catalyzed by the metallic ions. Semi-quantitative measurements indicate that the dehydrogenation reaction requires an energy of activation of about 17.5 k.cals. in excess of that for the dehydation reaction and that the energy of activation for the former case is slightly higher than that found for the decomposition of ethanol over metallic copper.

Further evidence of the catalytic effect of metal ions in the melt has been shown for a silver chloride melt. Solution of metallic silver in the melt appeared to increase the dehydogenation of ethanol, at the expense of the dehydration reaction.

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VITA

The author was born on February 18, 1923 at Bunbury, Western Australia. He attended public schools and gained a scholarship to Perth Modern School. In 1940 he entered the University of Western Australia and graduated with the Degree of Bachelor of Science in Chemistry in 1943. Receiving a Hackett Research Scholarship, he undertook further work in 1944 and 1945 for the Honours Degree in Technical Chemistry. The research was in connection with wartime projects. During the latter half of 1945 and in 1946 he was employed as a research chemist in the heavy chemical industry. In October 1946 he entered University College, London, and gained the Diploma of that College in Chemical Engineering in June 1947. He entered the University of Illinois in October 1947 and received the Degree of Master of Science in Chemical Engineering in June 1948. Since that time he has held a graduate teaching assistantship.